

# PATENT SPECIFICATION

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NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Gas Generation.

We, MINE SAFETY APPLIANCES COMPANY, a corporation organized under the laws of the State of Pennsylvania, United States of America, of 201 North Braddock Avenue, 5 Pittsburgh, Pennsylvania 15208, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to solid compositions that evolve hydrogen on heating.

There is a need, particularly in the field, 15 for a safe and convenient source of hydrogen for many purposes, for example, for balloon filling and welding. Hydrogen is generally carried in cylinders, which are cumbersome and a potential safety hazard, 20 or may be generated by solid-liquid reactions utilizing complex and inconvenient generating apparatus.

It is an object of this invention to provide improved hydrogen sources which 25 evolve the gas on heating. The sources of the invention are easily portable, safe and efficient.

The invention provides stable solid hydrogen-generating composition comprising an intimate mixture of, as a first compound, a finely divided metal hydride or borohydride or mixture thereof, and a finely divided second compound which yields free water on heating at a temperature below the decomposition temperature of the first compound, 35 the composition reacting to generate hydrogen on heating.

The compensation may be a loose mixture, suitably contained in canisters or bags, but preferably it is compressed under sufficient 40 pressure to form a coherent solid body such as a pellet.

[Price 4s. 6d.]

Catalysts are known to promote reaction in some systems, for example, the catalysis 45 by transition metal chlorides of the reaction of sodium borohydride or potassium borohydride with water and may be included in the mixtures.

The compounds used in the invention, which yield free water on heating at a temperature below and decomposition temperature of the first compound, will be stable at an easily obtainable storage temperature. The water in the compound is less firmly bound at elevated temperatures as is shown 50 by an increase in vapour pressure with increasing temperature. Generally, a higher vapour pressure indicates a greater availability of the combined water for reaction. Thus, compositions containing a water-reactive compound and a potentially reactive compound that yields free water on heating 60 may be stable at normal temperatures and reaction can be initiated simply by heating to make the combined water available for reaction. The temperature at which reaction is initiated may be adjusted by the selection of the water-containing compound those with a higher vapour pressure giving a 70 lower reaction temperature.

Suitable water-containing compounds include compounds containing coordinated water, compounds containing uncoordinated water of crystallisation, solvated compounds, 75 and other compounds in which the water is chemically combined.

Compounds containing coordinated water are those in which water molecules are attached to the metal atom of a salt in an orderly arrangement. Representative examples of such compounds include certain 80 metal chlorides such as  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  and  $\text{Sn}(\text{H}_2\text{O})_2\text{Cl}_4$ , and amphoteric hydroxides

such as  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CuO}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{Na}_2\text{ZnO}_2 \cdot 4\text{H}_2\text{O}$ .

Uncoordinated water of crystallisation is associated with a salt or hydroxide molecule and is not as firmly bound as coordinated water. Representative examples of compounds containing uncoordinated water include  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ .

It should be recognised that many compounds may contain both coordinated and uncoordinated water, for example, alums which contain 6 molecules of coordinated water and 6 molecules of uncoordinated water. Such compounds are suitable for use and, if desired, the uncoordinated water may be removed by dessication or heating before use in the compositions of this invention. Representative examples of compounds containing both coordinated and uncoordinated water include  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ .

Olated compounds are compounds in which metal atoms are joined by bridging OH groups and thus are sometimes referred to as hydroxides. Upon heating, however, olated compounds give up water and revert to oxy-metal compounds. Representative examples of olated compounds are the basic metal chlorides and sulphates such as  $\text{Cr}_2(\text{OH})_6\text{Cl}_2$  and  $[\text{Al}_2(\text{OH})_5]_2\text{SO}_4$ .

Other compounds that release or partially release free water on heating can also be used in this invention, for example, boric acid, and group IB, IIA and IIB metal hydroxides, for example calcium hydroxide (using the Periodic Classification of Mendeleef).

The invention provides a composition for the generation of hydrogen in which the first compound is sodium or potassium borohydride or a mixture thereof, and the second compound has a vapour pressure of less than 8 mm. of Hg at  $20^\circ\text{C}$ ., preferably of less than 4 mm. Hg at  $20^\circ\text{C}$ . It is preferred to use a stoichiometric amount of borohydride and water-containing compound (based on available water content) as such proportions give the highest yield of hydrogen per pound of gas-generating solid, and there is no advantage in using proportions other than stoichiometric.

#### Example I

9.5 g. of  $\text{NaBH}_4$ , 20.9 g. of  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and 0.5 g. of anhydrous  $\text{CoCl}_2$  were intimately mixed and compressed into a coherent pellet at 4000 psig. These pellets are stable at ordinary temperatures when protected from atmospheric moisture. When the pellets are heated to about  $130^\circ\text{F}$ . in a test tube having a gas outlet, hydrogen evolution commences and, once initiated, the reaction is self-sustaining without additional application of heat. A 98% yield of  $\text{H}_2$  of about

99% purity was evolved over a period of two minutes. Eleven cubic feet of hydrogen (STP) are produced for each pound of this gas generating composition.

#### Example II

9.5 g. of powdered  $\text{NaBH}_4$ , 22.5 g. of powdered  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  and 0.5 g. of anhydrous  $\text{CoCl}_2$  were compacted as in the previous example. The pellets, stable at ambient temperature, evolved substantially pure hydrogen in 85% yield from the self-sustaining reaction initiated by heating to about  $150^\circ\text{F}$ .

#### Example III

Pellets stable at ambient temperature containing 9.5 g.  $\text{NaBH}_4$ , 30 g.  $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$  (all water molecules being coordinated) and 0.5 g.  $\text{CoCl}_2$  gave a 98% yield of 99.9% pure hydrogen when reaction was initiated by heating to  $150^\circ\text{F}$ .

The major impurity in the hydrogen produced is water and the amount of water decreases with increasing density of the compact.

Any of the well-known solid catalysts for accelerating the reactions of borohydrides and water can be used, provided they do not contain any adsorbed water or water of crystallisation. Such catalysts include any acidic material, those materials of high acidity and water solubility being most effective. Transition metal chlorides, which appear to react with the borohydride to produce a highly active catalyst, are preferred catalysts. Representative examples of suitable catalysts include phthalic acid, salicylic acid, benzoic acid, sulphamic acid, oxalic acid, succinic acid, citric acid, tartaric acid, ammonium chloride, aluminium chloride, iron (II) chloride, cobalt (II) chloride, nickel (II) chloride, boric acid, acid sulphates and diacid phosphates.

When the water-reactive compound is highly reactive, for example, lithium borohydride ( $\text{LiBH}_4$ ), and calcium hydride ( $\text{CaH}_2$ ), only those water-containing materials containing no water of crystallisation and having a vapour pressure of less than 0.1 mm. of mercury at  $20^\circ\text{C}$ . can be used for example  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ , boric acid, and group IIA, IB and IIB hydroxides.

The following example generates one mole of hydrogen.

#### Example IV

21.05 g.  $\text{CaH}_2$  and 41.22 g.  $\text{H}_3\text{BO}_3$  are used to produce hydrogen. The reaction is initiated by heating to  $130^\circ\text{F}$  and is self-sustaining if heated to  $150$ — $160^\circ\text{F}$ .

#### WHAT WE CLAIM IS:—

1. A stable solid hydrogen-generating composition comprising an intimate mixture

- of, as a first compound, a finely divided metal hydride or borohydride or mixture thereof, and a finely divided second compound which yields free water on heating at a temperature below the decomposition temperature of the first compound, the composition reacting to generate hydrogen on heating.
2. A composition as claimed in claim 1 comprising, as a first compound, calcium hydride.
3. A composition as claimed in claim 1 comprising, as a first compound, lithium borohydride.
4. A composition as claimed in claim 1 comprising, as a first compound, sodium or potassium borohydride or mixture thereof.
5. A composition as claimed in claim 1 or 2 or 3 in which the second compound contains no water of crystallisation and has a vapour pressure below 0.1 mm. of mercury at 20°C.
6. A composition as claimed in claim 4, in which the second compound has a vapour pressure below 8 mm. mercury at 20°C.
7. A composition as claimed in claim 6 wherein the vapour pressure of the second compound is below 4 mm. mercury at 20°C.
8. A composition as claimed in any of claims 4 to 7 which also contains a minor amount of an anhydrous catalyst for accelerating the reaction of the borohydride(s) and water.
9. A composition as claimed in claim 8, in which the catalyst is acidic.
10. A composition as claimed in claim 8, in which the catalyst is cobalt (II) chloride.
11. A composition as claimed in any preceding claim in which the second compound contains coordinated water.
12. A composition as claimed in any of claims 4 or 6 to 10 in which the second compound contains uncoordinated water of crystallisation.
13. A composition as claimed in any of claims 1 to 10 in which the second compound is an related compound as herein defined.
14. A composition as claimed in claim 11 in which the second compound is  $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2$  or  $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$ .
15. A composition as claimed in any of claims 1 to 10 in which the second compound is boric acid.
16. A composition as claimed in claim 12 in which the second compound is  $\text{LiOH} \cdot \text{H}_2\text{O}$ .
17. A composition as claimed in any of claims 1 to 10 in which the second compound is a hydroxide of a metal from group IB, IIA or IIB of the Periodic Table of Mendeleef.
18. A composition as claimed in any preceding claim in the form of a coherent compact.
19. A composition as claimed in any preceding claim in which the composition reacts autogeneously.
20. A hydrogen-generating composition as claimed in claim 1 substantially as herein described.
21. A hydrogen-generating composition substantially as described in any of Examples I to IV.

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